Engineers
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December 6, 1984

S17705.B0

Mr. Melvin N. Miller
Monsanto Industrial Chemical Co.
9229 East Marginal Way South
P.O. Box 80963
Seattle, Washington 98108

Dear Mr. Miller:

Enclosed are three copies of our draft report concerning the Duwamish River water quality sampling program conducted in August 1984 near your facility. Please review this draft and return a copy with your comments. If you have any questions regarding this report please call.

Sincerely,

Donald R. Heinle

Donald R. Heinle, Manager
Environmental Sciences

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Enclosures

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SUMMARY

The Duwamish waterway was sampled at five sampling points on three consecutive days in August 1984. Three sampling points were from surface water while two points were subsurface in the salt wedge. Water was composited and sent to analytical laboratories for analysis of the 129 priority pollutants (except asbestos). Analysis was also done of several non-priority pollutant metals.

Negative results were obtained on all samples from analyses of volatiles, base/neutral compounds, acids, pesticides, PCB's, and cyanide. Nine priority pollutant metals were detected primarily from the salt wedge sampling points and the downstream surface sampling point. Eight metals were detected at greater amounts downstream than upstream in the surface waters.

INTRODUCTION

CH2M HILL was contracted by Monsanto to sample water from the Duwamish waterway in the vicinity of their Seattle plant and analyzed this water for the 129 priority pollutants and other water quality parameters. This report presents the sampling techniques, analytical protocol, and results of the priority pollutant and nonpriority pollutant analyses from the August 1984 sampling program.

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COLLECTION TECHNIQUE

Water was collected and composited from the Duwamish River adjacent to the Monsanto Seattle plant on August 28, 29, and 30, 1984. Three transect locations were sampled each day during the last 2 hours of a falling tide.

Tidal Heights

Date	Time	Height (ft)
August 28	12:39	-0.7 feet
August 29	13:24	0.2 feet
August 30	14:10	0.6 feet

On the dates of sampling, the U.S. Geological Survey gage at Tukwila showed flows of 498, 495, and 487 cfs (O. Heddig, USGS, personal communication).

Transects U and D were based on the Monsanto Seattle Plant Environmental Assessment--Priority Pollutants Report dated February 19, 1979 (Figure 1). A Hydrolab Model 8000 was used to determine the presence of a salt wedge in the river. Because saline water was detected at approximately 2 meters at midtransect D (downstream from the plant), subsurface samples were taken at transects D and U (upstream from the plant). A total of five samples was obtained:

- D1--surface sample, transect D
- D2--subsurface sample (sampling depth 4 meters), transect D
- U1--surface sample, transect U
- U2--subsurface sample (sampling depth 2 meters), transect U
- S1--surface sample, east side boat slip.

Transect D1 was composed of three sampling points: D1.1, D1.2, and D1.3 (Figure 1). Transect D2 was at the same location as sampling point D1.2 but was sampled at a depth of 4 meters. Transect U1 was composed of two sampling points, U1.1 and U1.2, with transect U2 being a subsurface (2 meters deep) single sampling point located midway between U1.1 and U1.2. Transect S1 was a surface transect composed of two sampling points at the mouth of Port of Seattle's boat slip on the east side of the river, along the southern boundary of the Monsanto plant.

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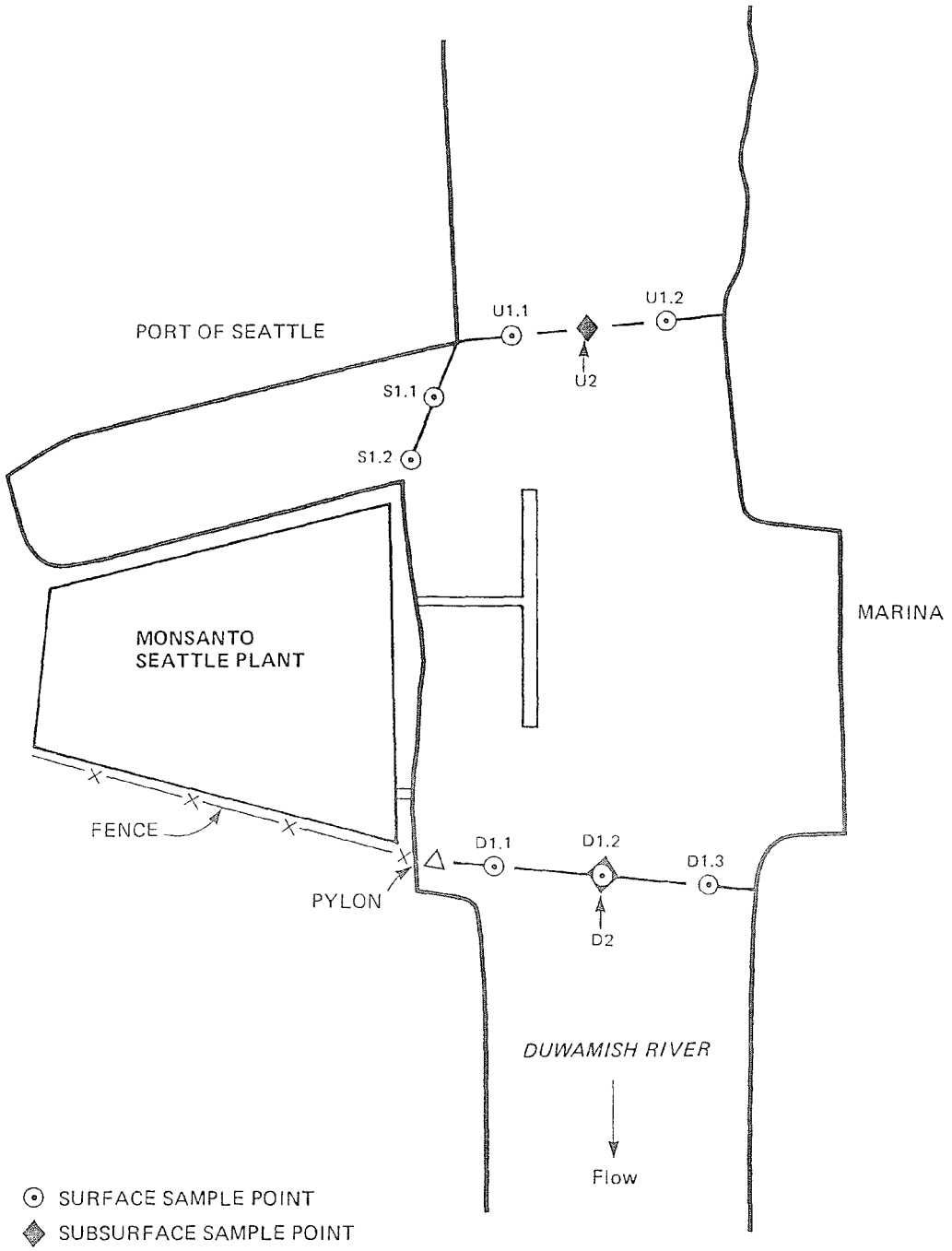

Figure 1
DUWAMISH RIVER
FIELD SAMPLING POINTS
AUGUST 1984

Samples were collected from an oar-powered, 13-foot Avon inflatable raft in the following order: D1, D2, S1, U1, U2. Surface water was collected from the upstream side of the raft. Calibrated glass jars with aluminum-covered lids (cleaned by CH2M HILL laboratories) were submerged 6 to 10 inches below surface waters, opened, and then relidded and retrieved. Subsurface samples were collected using a Teflon-coated Niskin bottle. Detailed trip notes including Hydrolab and conductivity/salinity analysis results are contained in Appendix A.

SAMPLE COMPOSITING TECHNIQUE

Calibrated glass jars were used to measure water samples for compositing. Composite containers were cleaned and prepared by the analytical laboratory doing analyses. Following is a list of collecting containers used in this study.

Analysis	Container	Laboratory
Priority pollutants (nonvolatile)	1/2-gallon amber glass bottle	CH2M HILL Montgomery
Priority pollutants (volatile)	Teflon-diaphragmed glass vials	CH2M HILL Montgomery
Metals--ICP	120-ml plastic vial	Amtest Inc.
Metals-atomic adsorption	Quart plastic cuvettes	CH2M HILL Corvallis
Cyanide	Quart plastic cuvettes	CH2M HILL Corvallis

Table 1 lists volumes of water collected each day from each transect and sampling point that comprised the total composite sample. Water collected in vials for volatile priority pollutant analysis was composited in the laboratory just prior to analysis.

SAMPLE STORAGE AND SHIPPING PROCEDURE

Samples were maintained in chain-of-custody control during this project. They were stored in ice chests and placed in a locked facility each night prior to shipping. Samples to be analyzed by CH2M HILL laboratories were shipped by Federal Express, and samples to be analyzed by Amtest were hand delivered following the completion of sampling.

Table 1
VOLUME OF WATER COLLECTED EACH DAY
FOR COMPOSITE SAMPLES
(ml unless otherwise noted)

Analysis	Laboratory	Transect D1			Transect D2	Transect U1		Transect U2	Transect S1		Transect Total Volume
		D1.1	D1.2	D1.3	D2	U1.1	U1.2	U2	S1.1	S1.2	
Priority pollutants	CH2M HILL (MGM)	150	300	150	600	300	300	600	300	300	2 liters
Volatiles	CH2M HILL (MGM)	2 vials	2 vials	2 vials	2 vials	2 vials	2 vials	2 vials	2 vials	2 vials	varied
Metals	CH2M HILL (CVO)	150	300	150	600	300	300	600	300	300	2 liters
CN	CH2M HILL (CVO)	75	150	75	300	150	150	300	150	150	1 liter
ICP Metals	Amtest	10	20	10	40	20	20	40	20	20	120 ml

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ANALYTICAL PROCEDURES

All tests were performed in accordance with current Environmental Protection Agency guidelines. Priority pollutants including volatiles, base/neutral compounds, acids, pesticides, and PCB's were analyzed using the following methodologies by the CH2M HILL Montgomery laboratory.

PRIORITY POLLUTANTS

The samples were analyzed in accordance with procedures described in Methods 608, 624, and 625, EPA-600/4-82-057 (1982).

Analytical instrumentations used in these analyses were the Finnigan Model 4021 Gas Chromatograph/Mass Spectrometer/Data System equipped with a Tekmar LSC-1 liquid sample concentrator and the Varian Model 3700 Gas Chromatograph equipped with flame ionization, electron capture, and thermionic specific detectors. Parameters analyzed for and corresponding method detection limits for these analyses are contained in Appendix Tables B-1 through B-4.

Methodology used by the CH2M HILL Corvallis laboratory for metals and cyanide analyses was as documented in the EPA reference Methods for Chemical Analysis of Water and Waste, No. 600/4-79-020, March 1979. Specific methods for the various elements and compounds were: Sb, 204.2; As, 206.2; Be, 210.1; Cd, 213.2; Cr, 218.2; Cu, 220.1; Pb, 239.2; Hg, 245.1; Ni, 249.1; Se, 270.2; Ag, 272.2; Tl, 279.1; Zn, 289.1; and Cn, 335.2.

Parameters analyzed for and method detection limits for these analyses are contained in Appendix Table B-5.

The multi-element Inductively Coupled Plasma Analysis (ICP) conducted by the Amtest Inc., Seattle, laboratory was conducted according to EPA Test Method 200.7 from EPA reference Methods for Chemical Analysis for Water and Waste, No. 600/4-79-020, dated March 1979. Parameters analyzed for and method detection limits for this analysis are listed in Appendix Table B-6.

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ANALYTICAL RESULTS

PRIORITY POLLUTANTS

Samples were analyzed for all 129 priority pollutants with the exception of asbestos. Results from volatiles, base/neutral compounds, acids, pesticides, and PCB's were all below method detection limits. The 13 priority pollutant metals were analyzed by flame, furnace, or cold vapor atomic adsorption (AA) by the CH2M HILL Corvallis laboratory. Eleven of these metals were also analyzed by furnace AA by the Amtest laboratory (Appendix Table B-6). Table 2 lists results from these priority pollutant metal analyses. Only those parameters found above the detection limit are listed. Cyanide levels in all samples were below detection limits.

Zinc levels measured by flame AA in the salt wedge samples ranged from 93 µg/l upstream to 139 µg/l downstream. These values are three to four times as high as STORET data reported by U.S. Army Corps of Engineers (1982), which showed the maximum zinc level in the Duwamish River at river mile 3.81 to be 39 µg/l (salinity of the sample not being listed). Surface zinc sample results from this survey were also high compared to the zinc levels from the CH2M HILL December 1983 sample program, the 1979 Monsanto report, as well as STORET data reported by U.S. Army Corps of Engineers (1982). Zinc is subject to salt matrix interference in analysis of seawater. Measured levels are enhanced in seawater.

In order to determine compliance with EPA's water quality criteria to protect freshwater aquatic life for cadmium, copper, nickel, and zinc, water hardness had to be determined. The following calculation provided in Standard Methods (page 195) was used to obtain a calcium carbonate equivalent in ppm (mg/l) for the three surface sample points:

Hardness, mg equivalent Ca CO_3/l = 2.497 [Ca, mg/l] + 4.118 [mg, mg/l]

ICP results were used in this calculation to obtain the following:

Station	Calcium Carbonate Equivalent (ppm)
D1	667
U1	264
S1	494
Average	475

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Downstream surface waters exceeded criteria for several parameters as shown in Table 2. Cadmium, copper, and zinc exceeded the 24-hour average concentration, and chromium exceeded the 24-hour average as well as the maximum concentration allowed. The eastside boat slip surface sample also exceeded the 24-hour average concentration criterion for cadmium, copper, and zinc, but concentrations were lower than at the downstream surface station.

NONPRIORITY POLLUTANTS

Thirteen nonpriority pollutant metals were analyzed by the Inductively Coupled Plasma Emission (ICP) method. Table 3 lists the results of this analysis. Appendix Table B-6 includes the detection limits for these parameters.

Sodium and magnesium were analyzed by flame AA in addition to the ICP method in order to better determine if there are deviations in the sodium-to-magnesium ratios expected from seawater. Seawater sodium and magnesium concentrations are expected to be approximate 10,561 ppm and 1,272 ppm, respectively. Their ratio is about 8.3:1. Results of sodium and magnesium analyses and corresponding ratios are presented in Table 4.

Table 2
RESULTS OF PRIORITY POLLUTANT METALS ANALYSIS
(µg/l)

Metal	Downstream Surface	Downstream Salt Wedge	Upstream Surface	Upstream Salt Wedge	East Side Slip Surface
Atomic Adsorption Method by CH2M HILL					
Antimony	9	38	<5	24	<5
Arsenic	<5	18	<5	5	<5
Cadmium	7.2	1.0	<0.5	0.7	0.7
Chromium (total)	41	12	<5	<5	<5
Copper	16	26	5	17	7
Mercury	0.06	<0.05	<0.05	<0.05	0.06
Nickel	130	34	<5	<5	<5
Thallium	100	300	<100	100	<100
Zinc	67	139	43	93	48
AA Method by Amtest					
Chromium	<1	<1	<1	35	<1
Copper	<1	33	<1	<1	<1
Zinc	<15	68	<15	<15	<15

Note: Only those detected are listed. Underlined concentrations are in excess of EPA criteria to protect freshwater aquatic life as listed below (µg/l).

	Hardness (mg/L)	24-hour Average (µg/l)	Maximum Concentration (µg/l)
Cadmium	264	.069	8.57
	475	.128	15.51
	667	.182	22.15
Chromium	NA	.29	21.0
Copper	264	5.6	55.2
	475	5.6	95.9
	667	5.6	132.0
Nickel	264	200	3,857
	475	312	6,027
	667	404	7,801
Zinc	264	47	719
	475	47	1,171
	667	47	1,552

NA = not applicable.

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Table 3
NONPRIORITY POLLUTANT ICP ANALYSIS RESULTS
(µg/l)

Parameter	Station: Downstream Surface	Downstream Salt Wedge	Upstream Surface	Upstream Salt Wedge	East Side Slip Surface
Barium	6	9	5	7	5
Boron	500	2,180	230	1,290	360
Calcium	52,200	195,000	25,500	122,000	40,100
Iron	560	380	710	490	670
Magnesium	130,000	605,000	48,100	362,000	95,200
Manganese	100	60	110	86	110
Phosphorus	1,810	1,580	1,400	1,570	1,570
Potassium	45,400	182,000	15,600	110,000	28,900
Silicon	14,900	7,550	16,600	11,100	15,400
Sodium	1,080,000	5,010,000	370,000	2,990,000	735,000
Strontium	840	3,640	310	2,220	600

Note: Only those detected are listed.

Table 4
NONPRIORITY POLLUTANT FLAME AA ANALYSIS RESULTS
(µg/l)

Parameter	Downstream Surface	Downstream Salt Wedge	Upstream Surface	Upstream Salt Wedge	East Side Slip Surface
Magnesium	134,000	492,000	40,700	251,000	78,600
Sodium	1,130,000	4,710,000	326,000	1,960,000	545,000
Sodium: Magnesium[a]	8.43:1	9.57:1	8.01:1	7.81:1	6.93:1

[a] Expected sodium: magnesium in seawater = 8.3:1.

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REFERENCES

U.S. Army Corps of Engineers. Draft Feasibility Report and Draft Environmental Impact Statement: East, West and Duwamish Waterways Navigation Improvement Study. 1982.

Hoogheem, Thomas J. Seattle Plant Environmental Assessment--Priority Pollutants. Monsanto Company Report MDA-028. 1979.

Standard Methods for the Examination of Water and Wastewater; Fifteenth Edition, 1980. Prepared and published by APHA, AWWA, abd WPCF. Washington, D.C.

Federal Register--November 28, 1980. Part V--Environmental Protection Agency: Water Quality Criteria Documents; Availability and Summary. (Revised - 46 FR156. August 13, 1981).

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APPENDIX A

TRIP NOTES AND FIELD DATA

TRIP NOTES

AUGUST 28, 1984

Weather: High overcast, calm waters, no wind. Low low slack at 1239.

Launched raft from marina dock across from Monsanto Plant. Rowed to Transect D and did Hydrolab profile at 1255. Hydrolab was not operating properly. Took surface temperature with hand-held thermometer. Saline waters present in subsurface waters determined by "taste test." Wedge identified at approximately 2 meters. Bottom was at 4.5 m. Sample obtained at 4 m. Collected samples in the following order: D2, D1.2, D1.3, D1.1. Proceeded to east side slip and sampled S1.1 and S1.2 at approximately 1400. Rowed to U1.1 and sampled followed by U2 and U1.2. Sampling time from 1415 to 1430 salt wedge at U2, also determined by taste test, occurred at approximately 1.5 meters. Bottom was at 2.5 meters. Sampled at 2 m. Samples were iced following returning to dock.

AUGUST 29, 1984

Weather: Sunny, light breeze rippled waters. Low low slack at 1324.

Hydrolab was repaired and profiles obtained at D2 and U2 (results in Table A-1). Sampling proceeded in the same order as during the preceding day. D2 sampled at 1315, D1 sampled from 1320 to 1330. S1 sampled at 1350. U2 sampled at 1410, and U1 sampled from 1400 to 1415. Samples were iced after returning to dock.

AUGUST 30, 1984

Weather: Slight high overcast, sunny, slight breeze. Low low slack at 1410.

Sampling proceeded the same as on August 29 with hydrolab profiles obtained at D2 and U2 (Table A-1). D2 sampled at 1405. D1 sampled from 1405 to 1420; S1 sampled at 1440. U2 sampled at 1450; U1 sampled from 1445 to 1500. Samples were iced after returning to dock. Samples shipped to CH2M HILL laboratories were sent by Federal Express the afternoon of August 30, 1984. Amtest samples for ICP analysis were hand delivered to Amtest the morning of August 31.

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Table A-1
WATER QUALITY RESULTS, DUWAMISH RIVER AT MONSANTO, AUGUST 1984

Date	Station	Depth (meters)	Temp (°C)	Conductivity[a] (micromhos)	Salinity[a] 0/00	pH[a]	Conductivity[b] (micromhos)	Salinity[b] (0/00)	pH[b]
8/28	D2	Surface	18.0	-	-	-	-	-	
8/29	D2	Surface	17.3	3,900	2.44	7.2			
		1	17.3	9,500	6.33	7.0			
		2	16.0	17,700	12.85	7.0			
		3	15.9	20,900	15.45	7.2			
		4	14.4	41,100	33.88	7.4			
		4.5 (bottom)	13.8	44,100	37.24	7.5			
	U2	Surface	17.5	1,700	0.99	7.6			
		1	17.2	3,000	1.84	7.2			
		2	16.9	10,400	7.05	7.0			
		3	15.6	25,100	19.03	7.2			
		3.5 (bottom)	14.7	38,500	31.26	7.4			
8/30	D2	Surface	17.5	9,100	6.01	7.1			
		1	17.0	13,400	9.25	7.0			
		2	16.8	19,700	14.16	7.0			
		3	16.5	24,500	18.12	7.2			
		4	14.1	41,600	34.61	7.4			
		5	14.0	43,200	36.20	7.5			
		6 (bottom)	13.8	44,500	37.62	7.5			
	U2	Surface	18.5	3,400	2.08	7.1			
		1	17.7	6,200	3.96	7.0			
		2	17.4	12,300	8.35	6.8			
		3	15.1	29,600	23.12	6.9			
		4 (bottom)	14.7	41,600	34.08	7.4			
Composite	D1	Surface					6,000	3.23	7.1
	D2	L/M					25,000	15.18	7.3
	S1	Surface					3,800	1.98	6.9
	U1	Surface					2,010	0.99	6.9
	U2	2 m					12,500	7.12	7.2

[a] Measured with a hydrolab model 8000 in field.

[b] Measured by CH2M HILL Corvallis laboratory.

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APPENDIX B

ANALYTICAL DETECTION LIMITS

Table B-1
BASE/NEUTRAL COMPOUNDS ANALYZED FOR AND METHOD DETECTION LIMIT
(Parts per billion or ppb equivalent to µg/l)

Compounds	Method Detection Limit (ppb)	Compounds	Method Detection Limit (ppb)
Bis (2-chloroethyl) ether	10	4-Bromophenyl phenyl ether	10
1,3-Dichlorobenzene	10	Hexachlorobenzene	10
1,4-Dichlorobenzene	10	Phenanthrene	10
1,2-Dichlorobenzene	10	Anthracene	10
Bis (2-Chloroisopropyl) ether	10	Dibutyl phthalate	10
Hexachloroethane	10	Fluoranthene	10
N-nitroso-di-n-propylamine	10	Pyrene	10
Nitrobenzene	10	Benzidine	40
Isophorone	10	Butyl benzyl phthalate	10
Bis (2-chloroethoxy) methane	10	2,3,7,8-Tetrachlorodibenzo-p-dioxin	10
1,2,4-Trichlorobenzene	10	Benzo (a) anthracene	10
Naphthalene	10	Chrysene	10
Hexachlorobutadiene	10	3,3'-Dichlorobenzidine	40
Hexachlorocylopentadiene	10	Bis (2-ethylhexyl) phthalate	10
2-Chloronaphthalene	10	Di-n-octyl phthalate	10
Acenaphthylene	10	Benzo (b) fluoranthene	10
Dimethylphthalate	10	Benzo (k) fluoranthene	10
2,6-Dinitrotoluene	10	Benzo (a) pyrene	10
Acenaphthene	10	Indeno (1,2,3-cd) pyrene	10
2,4-Dinitrotoluene	10	Dibenzo (a,h) anthracene	10
Fluorene	10	Benzo (g,h,i) perylene	10
4-Chlorophenyl phenyl ether	10	N-nitrosodimethylamine	ND
Diethyl phthalate	10	Bis (chloromethyl) ether	ND
N-nitrosodiphenylamine	10		
1,2-Diphenylhydrazine	10		

ND = not determined.

Table B-2
ACID COMPOUNDS ANALYZED FOR AND METHOD DETECTION LIMIT
(Parts per billion or ppb equivalent to µg/l)

Compounds	Method Detection Limit (ppb)
Phenol	10
2-Chlorophenol	10
2-Nitrophenol	10
2-4-Dimethylphenol	10
2-4-Dichlorophenol	10
4-Chloro-3-methylphenol	10
2,4,6-Trichlorophenol	10
2,4-Dinitrophenol	50
4-Nitrophenol	10
2-Methyl-4,6-dinitrophenol	50
Pentachlorophenol	10

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Table B-3
VOLATILE COMPOUNDS ANALYZED FOR AND
METHOD DETECTION LIMIT
(Parts per billion or ppb equivalent to µg/l)

Compounds	Method Detection Limit (ppb)
Chloromethane	10
Bromomethane	10
Vinyl chloride	10
Chloroethane	10
Methylene chloride	5
Trichlorofluoromethane	5
1,1-Dichloroethene	5
1,1-Dichloroethane	5
Trans-1,2-Dichloroethene	5
Chloroform	5
1,2-Dichloroethane	5
1,1,1-Trichloroethane	5
Carbon tetrachloride	5
Bromodichloromethane	5
1,2-Dichloropropane	5
Trans-1,3-Dichloropropene	5
Trichloroethylene	5
Benzene	5
Dibromochloromethane	5
1,1,2-Trichloroethane	5
Cis-1,3-Dichloropropene	5
2-Chloroethyl vinyl ether	10
Bromoform	5
1,1,2,2-Tetrachloroethane	5
Tetachloroethylene	5
Toluene	5
Chlorobenzene	5
Ethyl benzene	5
Acrylonitrile	100
Acrolein	100
Dichlorodifluoromethane	ND[a]

[a] ND = not determined.

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Table B-4
PESTICIDES/PCB's ANALYZED FOR AND METHOD DETECTION LIMIT
(Parts per billion or ppb equivalent to µg/l)

Compounds	Method Detection Limit (ppb)
Aldrin	0.2
a-BHC	0.2
b-BHC	0.2
d-BHC	0.2
g-BHC	0.2
Chlordane	0.5
4,4'-DDD	0.2
4,4'-DDE	0.2
4,4'-DDT	0.2
Dieldrin	0.2
Endosulfan I	0.2
Endosulfan II	0.2
Endosulfan sulfate	0.5
Endrin	0.2
Endrin aldehyde	0.5
Heptachlor	0.2
Heptachlor epoxide	0.2
Toxaphene	3.0
PCB-1016	2.0
PCB-1221	2.0
PCB-1232	2.0
PCB-1242	2.0
PCB-1248	2.0
PCB-1254	2.0
PCB-1260	2.0

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Table B-5
METALS ANALYZED BY ATOMIC ADSORPTION
METHODOLOGY AND DETECTION LIMIT

Metal	Detection Limit (µg/l)	AA Method Used[1]
Antimony	5	A
Arsenic	5	A
Beryllium	10	B
Cadmium	0.5	A
Chromium (total)	5	A
Copper	-	A
Cyanide	20	-
Lead	5	A
Magnesium	-	B
Mercury	0.05	C
Nickel	5	A
Selenium	5	A
Silver	1	A
Thallium	100	B
Zinc	5	B

[1] A = graphite furnace AA.
B = direct flame AA.
C = cold vapor AA.

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Table B-6
PARAMETERS ANALYZED FOR BY ICP AND FURNACE AA METHODOLOGY
BY AMTEST LABORATORY AND DETECTION LIMITS

Parameter		Method	Detection Limit (µg/l)
Aluminum	Al	ICP	150
Antimony[a]	Sb	AA	5
Arsenic[a]	As	AA	1
Barium	Ba	ICP	1
Beryllium[a]	Be	AA	3
Bismuth	Bi	ICP	500
Boron	B	ICP	10
Cadmium[a]	Cd	AA	1
Calcium	Ca	ICP	10
Chromium[a]	Cr	AA	1
Cobalt	Co	ICP	20
Copper[a]	Cu	AA	1
Iron	Fe	ICP	30
Lead[a]	Pb	AA	1
Magnesium	Mg	ICP	1
Manganese	Mn	ICP	3
Molybdenum	Mo	ICP	40
Nickel[a]	Ni	AA	5
Phosphorus	PO_4	ICP	400
Potassium	K	ICP	10
Silicon	SiO_2	ICP	80
Silver[a]	Ag	AA	1
Sodium	Na	ICP	100
Strontium	Sr	ICP	1
Thallium[a]	Tr	AA	5
Tin	Sn	ICP	30
Titanium	Ti	ICP	6
Vanadium	V	ICP	10
Zinc[a]	Zn	AA	15

[a]Priority pollutant.

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